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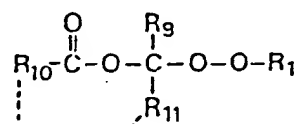
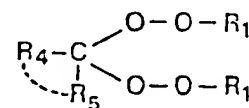
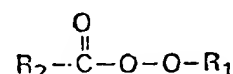
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⑤④ **Process for cross-linking shaped non-polar synthetic resins and electric objects insulated with said crosslinked resins.**

⑤⑦ Non-polar synthetic resins are cross-linked by mixing the resin with a peroxide having a formula illustrated in the accompanying drawing and exposing the mixture to a high frequency alternating current field in the absence of any polar auxiliary substance other than said peroxide.

The polymers thus cured have favourable electrical properties and are very suitable to be used as insulating material for electrical cables.



EP 0 009 268 A1

Process for cross-linking shaped non-polar synthetic resins and electric objects insulated with said crosslinked resins.

The invention relates to a process for cross-linking shaped non-polar synthetic resins by bringing them in a high frequency alternating current field in the presence of a polar peroxide and in the absence of a polar auxiliary substance.

A process of the type indicated above is known from the German Patent Application DE-OS 2 611 349. According to the process described in said publication use is made of compounds that are unstable in a high frequency alternating current field, such as peroxides and azo compounds which are sufficiently polar to decompose into radicals in a high frequency alternating field or, if they are not unstable, do decompose into radicals in the presence of an auxiliary substance which does get activated by the alternating current field. In the publication no specific peroxides, azo compounds or auxiliary substances are mentioned. Applicant has found that in the absence of an auxiliary substance which in itself is undesirable, acceptable results can be obtained only with the use of very special polar peroxides, other polar peroxides being unsuitable for use in actual practice. Polarity is a necessity but by no means the only requirement. Not only the symmetrical peroxides such as dicumyl peroxide and ditertiary peroxide are, as was to be expected, inactive, but there are also polar peroxides which do not give satisfactory results. Their use, even in relatively large amounts, leads to the following polar peroxides not being cross-linked at all or only to a quite insufficient degree:

tert. butyl hydroperoxide;
tert. butyl cumyl peroxide;
cumene hydroperoxide;
mono tert. butylperoxy-maleinate;
4-tert. butylperoxy-4-methyl-2-pentanone;
cumylperoxy-trimethyl silane;
tert. butylperoxy-stearyl carbonate
tert. butylperoxy-cetyl carbonate;
2,2-bis cumylperoxy-propane;
2,2-bis (4,4- di-t. butylperoxy-cyclohexyl)propane;

- 2 -

1-ethyl carboxymethylene-1,4,4',7,7'-pentamethyl-2,3,8,9-tetraoxa-cyclononane.

Other polar peroxides do result in cross-linking, but they are unfit for use in that they become active already during the initial shaping stage and cause the polymer to be cross-linked before it is in its final form, so that it becomes unprocessable (scorching).

Examples thereof include:

- tert. butylperoxy-p-methoxybenzoate;
- tert. butylperoxy-(2,2-diethyl acetate);
- tert. butylperoxy-2-ethyl hexanoate;
- cumylperoxy-hexahydrobenzoate;
- dicumylperoxy-hexahydroterephthalate;
- tert. butylperoxy-pivalate.

There are also polar peroxides which during the cross-linking reaction emit quite an amount of gas, which is occluded in the material so that it becomes unsuitable for electrical insulation purposes. Examples thereof include:

- tert.butylperoxy-(2,2 diethyl)acetate;
- cumyl perbenzoate;
- cumyl percaprylate.

It has now been found that with the use of a process of the type indicated above as known favourable results are obtained if as peroxide there is used a compound selected from the following group:

- A: peresters of the general formula 1, 1a or 2;
- B: perketals of the general formula 3 or 4;
- C: peroxides of the general formula 5

where the letters R have the following meaning:

- R1: a tertiary alkyl group having 4-12 carbon atoms; and in the case of peroxides of the formula 5, a tertiary alkyl group having 4-12 carbon atoms or a tertiary aralkyl group having 7-12 carbons atoms.
- R2: a primary alkyl group having 1-12 carbon atoms, or an aryl group having 7-12 carbon atoms and substituted with one or more methyl groups; and in the case of peroxides having the formula 1a, also alternatively a phenyl group.

- 3 -

R3: a primary alkylene group having 1-12 carbon atoms, a vinylidene group or a phenylene group;

R4 and R5: primary alkyl groups having 1-12 carbon atoms or together with the adjacent carbon atom forming part of a cyclopentamethylene group or cyclohexamethylene group which may or may not be methyl-substituted;

R6: a diprimary alkylene group having 1-12 carbon atoms or together with the adjacent carbon atoms and R7 and R8 forming part of a cyclopentamethylene group or cyclohexamethylene group which may or may not be methyl-substituted.

R7 and R8: primary alkyl groups having 1-12 carbon atoms or together with the adjacent carbon atoms and R6 forming part of a cyclopentamethylene group or cyclohexamethylene group which may or may not be methyl-substituted;

R9: a methyl group or phenyl group;

R10 and R11: primary alkyl groups having 1-12 carbon atoms, cyclopentyl groups or cyclohexyl groups, aryl groups or

together and along with the adjacent $\begin{array}{c} \text{O} \quad \text{R9} \\ \parallel \quad | \\ -\text{C}-\text{O}-\text{C}- \end{array}$ group forming part of a substituted or unsubstituted ring system having 5 or 6 atoms in the ring;

R12: a ditert. alkylene group having 8-12 carbon atoms.

If use is made of these peroxides, the above drawbacks are not met and products having excellent properties are obtained.

The process according to the invention is specially of importance for the manufacture of insulated electric objects, more particularly electric wires.

Electric conductors are generally insulated with polymers and copolymers of olefins such as ethylene. Because of their non-polar character these polymers are very suitable to be used as electric insulating material, but they do not readily cross-link in a high frequency alternating current field in the presence of the usual radical initiators because the polymer itself is not heated by the field. For that reason, as appears from the Netherlands Patent

Application NL 274 239 and the German Patent Application DE-OS 2 611 349, polar substances (such as carbon black) which absorb energy from the high frequency alternating current field are sometimes added to these polymers, which substances heat the polymer and thus

- 4 -

indirectly activate the radical initiators. In that way the polymers are in fact artificially polarized, which is inadmissible for electrical insulation purposes in the intermediate and in the high voltage range.

5 In practice, for the purpose of cross-linking the polymers, electric objects such as cables insulated with such polymers are, upon being shaped, heated to a temperature at which the radical initiators present in the polymer are activated and hence caused to bring about cross-linking. To that end the cables are passed through very long ovens in
10 which they are heated to the desired temperature with the aid of steam or nitrogen under pressure. This method of cross-linking not only has the disadvantage that it is costly due to the very intricate technology, but also the cables becoming damp when use is made of steam is considered a great drawback. Moreover, there is the side effect
15 then of the formation of closed voids. In the process according to the invention the polymer provided with a coating (containing the peroxide) is passed through ovens in which a high frequency alternating current field is maintained by which the polymer is cross-linked. The length of these ovens is far shorter than that of the ones that are commonly
20 employed. The electrical properties of the products according to the invention compare with those of the best products obtained by the prior art processes. A particularly suitable compound is di-tert. butyl peroxy terephthalate (formula 8). Also very suitable are compounds having the general formula (5) of the formula sheet, such as 2-methyl-
25 2 cumylperoxy-5-ketotetra-hydrofuran (formula 7) and 3-phenyl-3-tert. butylperoxy-phthalide (formula 6). These compounds and their method of preparation are described in US 3,654,315

The amount of polar peroxyde to be used may vary between wide limits. In general, excellent results are obtained with an amount of 5 per cent
30 by weight, although often good results may be obtained with the use of smaller amounts. High frequency alternating current fields are known in the art and the apparatus for creating them is commercially available. The frequency of a suitable field may be for instance: 434, 915 or 2450 Mhz.

35 The process according to the invention also may be successfully applied to non-electrical objects.

- 5 -

The process offers particularly advantages for objects having a high wall thickness because in that case heating methods other than by high frequency give rise to non-homogeneous rises in temperature in the object.

5 Besides the process described, the invention comprises the products obtained with it.

The invention will be further described in the following examples:

Examples 1-23.

10 On a two-roll mill the peroxide used was mixed with polyethylene powder (Alkathene 017040, registered trade mark of ICI) at a temperature of 120°C. Of this mixture 200 grammes were immediately afterwards exposed for 5 minutes to high frequency radiation of 2450 Mhz (1000 W). In all cases the degree of cross-linking was measured both before and after radiation by extraction for 6 hours
15 with boiling xylene. The results are given as the weight fraction of non-extracted (= cross-linked) polymer (gel fraction). Results acceptable for practical purposes are obtained if more than about 60% of the material is not extracted.

In this way the following peroxides were examined for their effective-
20 ness. In brackets are mentioned for a number of peroxides the trade name under which the product is marketed by Akzo Chemie b.v. and their representative general formula of the formula sheet.

1. dicumyl peroxide (Perkadox SB);
2. tert. butyl cumyl peroxide (Trigonox T);
- 25 3. tert. butyl hydroperoxide (Trigonox A);
4. tert. cumene hydroperoxide (Trigonox K);
5. tert. butylperoxy-(p.methoxy) benzoate;
6. tert. butylperoxy-(2,2-diethyl acetate) (Trigonox 27);
7. cumyl perbenzoate;
- 30 8. cumyl percaprylate;
9. 2,2-bis (4,4-di-tert. butylperoxy-cyclohexyl) propane (Perkadox 12);
10. 2,2-biscumylperoxy-propane;
11. tert. butylperoxy-stearyl carbonate;
12. tert. butylperoxy cetyl carbonate;
- 35 13. mono-tert. butylperoxy-maleinate;
14. 1-ethyl carbomethylene-1,4,4',7,7'-penta-methyl-2,3,8,9-tetraoxa-cyclononane;

- 6 -

15. 4-tert. butylperoxy-4-methyl pentanone-2;
16. 2,5-di-tert. butylperoxy-2,5-dimethyl-tetrahydrofuran;
17. cumylperoxy-trimethylsilan;
18. tert. butylperoxy-3,5,5-trimethyl hexanoate (Triganox 42S,
5 formula 1);
19. 2,5-dibenzoylperoxy-2,5-dimethyl hexane (formula 1a);
20. di-tert. butylperoxy terephthalate (formula 2 and 8);
21. 1,1-di-t-butyl peroxy-3,5,5-trimethyl-cyclohexane (Triganox 29,
formula 3);
- 10 22. 2-methyl 2-cumyl peroxy 5-ketotetrahydrofuran (formula 5 and 7);
23. 3-tert. butylperoxy-3-phenylphthalide (formula 5 and 8).

The results are given in the following table. In all cases the amount of peroxide was 5% by weight.

- 7 -

Experiments leading to results which were unacceptable for practical purposes.

Table I

5	Experiments with peroxide	gel fraction (%)		Observations
		before	after	
		radiation		
10	1	0	0	no cross-linking
	2	0	0	ditto
	3	0	0	ditto
	4	0	0	ditto
	5	45	95	cross-linking even before radiation
	6	40	40	cross-linking and occlusion of gas bubbles even before radiation
	7	0	73	much occlusion of gas
	8	0	54	occlusion of gas and insufficient cross-linking
15	9	0	8	hardly any cross-linking
	10	0	0	no cross-linking
	11	0	16	insufficient cross-linking
	12	0	29	ditto

Table II

20	Experiments with peroxide	results
25	13	hardly any cross-linking
	14	no cross-linking
	15	hardly any cross-linking
	16	too little cross-linking
	17	no cross-linking

- 8 -

Experiments according to the invention leading to results acceptable for practical purposes.

Table III

Experiments with peroxide	gel fraction (%)		Observations
	before	after	
	radiation		
18	0	70	over curing little rise in temperature over curing
19	~ 0	65	
20	0	95	
21	0	60	
22	0	83	
23	0	98	

Examples 24 - 26

The above experiments were repeated with di-t-butyl peroxy terephthalate (20), 2-methyl 2 cumylperoxy -5-ketotetrahydrofuran (22) and 3-tert. butylperoxy-3-phenylphthalide (23), but in such a way that these peroxides were added in an amount of only 2 or 3% by weight.

Experiments with peroxide	wt % peroxide	gel fraction (%)	
		before	after
		radiation	
20	2	0	65
22	3	0	60
23	2	0	73

These examples show that a satisfactory degree of cross-linking also can be obtained when use is made of small amounts of peroxide. The use of small amounts of peroxide is, of course, attractive for economic reasons, but it has the additional advantage that in the cross-

- 9 -

linked polymer only very little foreign substance is left, which has a particularly favourable effect on the electrical properties.

Example 27

On a two-roll mill, over a period of 3 minutes and at 100°C, 3-t-butylperoxy-3-phenylphthalide (23) was mixed with EPDM rubber (Keltan 520, registered trade mark of DSM). The mixture contained 2% by weight of peroxide. Of this mixture 200 grammes were immediately afterwards exposed for 5 minutes to high frequency radiation of 2450 MHz (1000 W). The degree of cross-linking was determined in the same way as described above for polyethylene. After radiation the degree of cross-linking was found to be 85%. This experiment demonstrates that also when use is made of ethylene-propylene terpolymers instead of polyethylene favourable results may be obtained.

C L A I M S

1. A process for cross-linking shaped non-polar synthetic resins by bringing them in a high frequency alternating current field in the presence of a polar peroxide, and in the absence of a polar auxiliary substance characterized in that as peroxide there is used a compound selected from the following group:

A: peresters of the general formula 1, 1a or 2;

B: perketals of the general formula 3 or 4;

C: peroxides of the general formula 5

where the letters R have the following meaning:

R1: a tertiary alkyl group having 4-12 carbon atoms; and in the case of peroxides of the formula 5, a tertiary alkyl group having 4-12 carbon atoms or a tertiary aralkyl group having 7-12 carbon atoms;

R2: a primary alkyl group having 1-12 carbon atoms, an aryl group having 7-12 carbon atoms and substituted with one or more methyl groups; and in the case of peroxides of the formula 1a, also alternatively a phenyl group;

R3: a primary alkylene group having 1-12 carbon atoms, a vinylidene group or a phenylene group;

R4 and R5: primary alkyl groups having 1-12 carbon atoms or together with the adjacent carbon atom forming part of a cyclopentamethylene group or cyclohexamethylene group which may or may not be methyl-substituted;

R6: a diprimary alkylene group having 1-12 carbon atoms or together with the adjacent carbon atoms and R7 and R8 forming part of a cyclopentamethylene group or cyclohexamethylene group which may or may not be methyl-substituted.

R7 and R8: primary alkyl groups having 1-12 carbon atoms or together with the adjacent carbon atoms and R6 forming part of a cyclopentamethylene group or cyclohexamethylene group which may or may not be methyl-substituted;

R9: a methyl or phenyl group;

R10 and R11: primary-alkyl groups having 1-12 carbon atoms, cyclopentyl groups or cyclohexyl groups, aryl groups or

together and along with the adjacent $\begin{array}{c} \text{O} \quad \text{R9} \\ \parallel \quad | \\ \text{-C-O-C-} \end{array}$ group

-11-

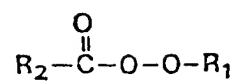
forming part of a substituted or unsubstituted ring
system having 5 or 6 atoms in the ring;

R12: a ditert. alkylene group having 8-12 carbon atoms.

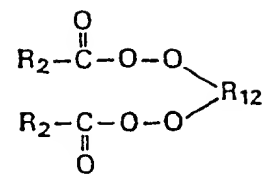
2. A process according to claim 1, characterized in that use is made
5 of di-tert.butylperoxyterephthalate (formula 8).
3. A process according to claim 1, characterized in that use is made
of 2-methyl-2-cumylperoxy-5-ketotetrahydrofuran (formula 7).
4. A process according to claim 1, characterized in that use is made
of 3-t-butylperoxy-3-phenyl phthalide (formula 6).
- 10 5. An electric object insulated with a crosslinked non-polar synthetic
resin obtained according to the process of any one of the preceding
claims.

1/21

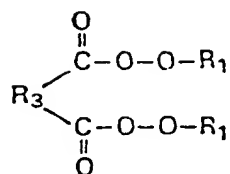
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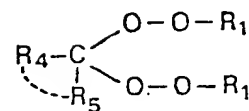
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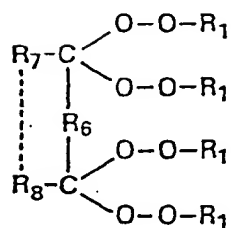
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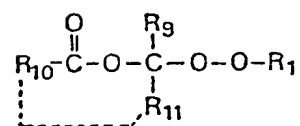
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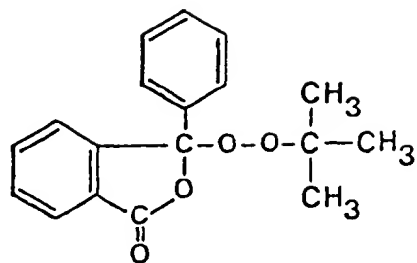
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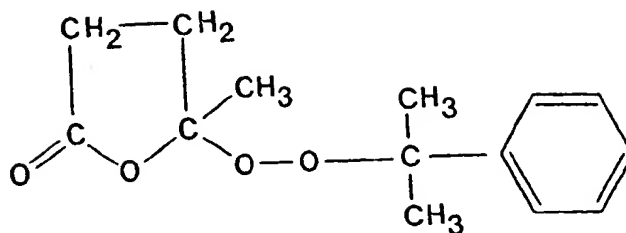


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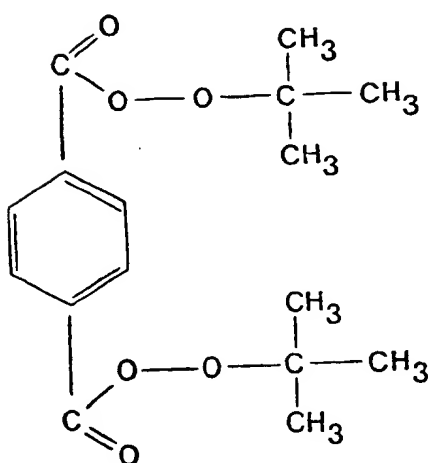


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European Patent
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EUROPEAN SEARCH REPORT

Application number
EP 79 20 0459

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	GB - A - 1 267 868 (PEROXID-CHEMIE) * Claims *	1	C 08 K 5/14 C 08 J 3/24 H 01 B 3/44
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	GB - A - 1 182 703 (KABEL- UND METALLWERKE GUTEHOFFNUNGSHUTTE) * Claims *	1	
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D, A	GB - A - 956 808 (DEGUSSA) * Claims *	1	C 08 K 5/14 C 08 J 3/24
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	GB - A - 1 276 758 (MONTECATINI) * Claims *	1	
	--		
P	US - A - 3 654 315 (YUN GER CHANG) * Column 1, lines 38-40 *	1-4	C 08 K 5/14 C 08 J 3/24
	GB - A - 2 013 213 (TROESTER) * Claims *	1-5	

			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same patent family, corresponding document
<input checked="" type="checkbox"/> The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 13-12-1979	Examiner LENSEN

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